Etching of indium tin oxide in methane/hydrogen plasmas

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The reactive ion etching of the transparent conductor, indium tin oxide (ITO), in methane/hydrogen plasmas has been characterized. It is shown that ITO can be selectively etched on GaAs and AlGaAs. Anisotropic structures and gratings with submicrometer dimensions in ITO are presented. Application of the etching process to the fabrication of highly sensitive metal–semiconductor–metal (MSM) photodetectors with interdigitated ITO fingers is demonstrated.

I. INTRODUCTION

Photodetectors are essential to the realization of high-speed optoelectronic integrated circuits and systems. These devices are either based on Schottky barrier or on PIN diode structures. An advantage of the Schottky barrier approach is the relative ease with which it can be fabricated. However, a major disadvantage is the low efficiency associated with the semitransparent metal contact layer.[1] The transparency of the metal contact layer is such that the percentage transmission of optical radiation to the underlying semiconductor is degraded. To overcome this efficiency problem, the use of indium tin oxide (ITO) as the contact layer has been proposed.[2] ITO is a transparent conductor that forms nearly ideal Schottky diode characteristics ($\Phi_B = 0.85$ eV, $n = 1.05$) on n-type GaAs. A class of Schottky barrier photodetectors is the highly integrable metal–semiconductor–metal (MSM) devices, which utilize interdigitated metallic fingers to form back-to-back Schottky diodes.[3] For a MSM device with one to one metal line to space ratio, optical transmission into the semiconductor cannot be more than 50%. Therefore, the use of a transparent conductor such as ITO should significantly improve its sensitivity. Zirngibl *et al.*[4] have made an initial demonstration of a sensitive interdigitated MSM photodetector using ITO finger metallization. The ITO used in this device was patterned by the liftoff process.

It has been shown that high quality ITO can be sputter deposited from indium oxide–tin oxide composite targets.[5] To pattern the deposited ITO film, a reliable etching method is required. Although buffered hydrofluoric acid (BHF) can be used to etch large geometries in ITO, this wet chemical etching process is inadequate for the micron-sized interdigitated lines needed for high speed MSM detectors. Recent results have shown that methane-based plasmas are versatile tools for etching InP and related compounds.[6,7] However, pattern formation in ITO using methane plasmas has not been investigated.

In this paper, we report the etching characteristics of ITO in methane/hydrogen (CH_4/H_2) plasmas. Etch rates and etch profiles as functions of various plasma parameters will be presented and discussed. It is shown that selective etching of ITO on GaAs can be achieved under appropriate plasma conditions. Finally, results on the application of etched interdigitated ITO fingers for MSM detectors are presented.

II. EXPERIMENTAL PROCEDURE

The ITO films used in this work were prepared by dc magnetron sputtering of a nominally 91 mol % In_2O_3:9 mol % SnO_2 composite target onto clean GaAs substrates at room temperature. X-ray photoelectron spectroscopy showed a 2.5% SnO_2 incorporation in the deposited ITO films.

A commercial planar diode RIE system manufactured by Plasma Technology and operated at 13.56 MHz was utilized in this work. The anode and cathode diameters were 30 and 17 cm, respectively. They were spaced 5 cm apart with the cathode water cooled and kept nominally at 24 °C during etching. The total gas flow rate was kept constant at 40 SCCM and the chamber pressure was controlled by a throttle valve.

Mask materials used were Al and photoresist. Etch rates were measured using a Tencor α-step surface profilometer. Submicrometer lines and gratings were defined using Cambridge EBMF 6.5 electron beam lithography system. Etch profiles were evaluated using a scanning electron microscope.

III. RESULTS AND DISCUSSION

A. Etch rates

Figure 1 shows ITO and GaAs etch rate dependence on the percentage of methane in CH_4/H_2 gas mixture at a pressure of 30 mTorr and a rf power of 100 W. The self-bias voltage at this pressure and power for the different gas mixtures was approximately 410 V. It is well known that the formation of thin films of polymer on surfaces is a byproduct of reactive ion etching in methane-based plasmas.[6-8] Therefore, polymer deposition rate on GaAs obtained during etching is shown in Fig. 1. The ITO etch rate increases rapidly at low CH_4 percentage, saturates at 40% CH_4, and decreases above 75% CH_4 concentration. For GaAs, the etch rate increases to a maximum of 8 nm/min at 10% CH_4 concentration and decreases thereafter to practically zero above 50% concentration. The shape of the GaAs etch rate curve agrees with that obtained by Cheung *et al.*[9] The etching character-

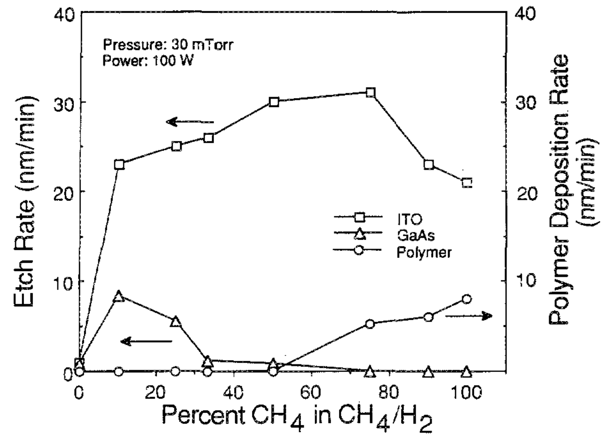


FIG. 1. Etch rates of ITO and GaAs and polymer deposition rate versus percentage methane concentration.

istics are influenced by polymer formation in the plasma. As shown, polymer deposition on GaAs become significant beyond 50% CH_4 concentration, which is where the etching of GaAs essentially stops. The oxygen in ITO provides a reaction path for eliminating some of the carbon in the form of gaseous CO_x. This allows ITO to be etched at reasonable etch rates for all CH_4 concentrations at 30 mTorr. However, the etch rate of ITO diminishes at CH_4 concentrations above 75% due to increasing polymer formation and deposition.[6-9] The deposited polymer is easily removed in an oxygen plasma. It is evident from Fig. 1 that ITO can be etched selectively on GaAs. The selectivity ranges from approximately 3 at 10% CH_4 to 300 at 50% CH_4 concentration. Above 50%, the selectivity is essentially infinite due to polymer formation on GaAs. The surface morphology of ITO was smooth under all conditions except at 100% CH_4 concentration due to uneveness of polymer deposition.

Figures 2 show the data on etch rate versus pressure for a gas composition of 25% CH_4 at a rf power of 100 W. Polymer deposition rate is also shown. The self-bias voltage decreases from 430 V at 20 mTorr to 330 V at 150 mTorr. The ITO etch rate increases from 24 nm/min at 20 mTorr to 35 nm/min at 150 mTorr. It is observed that although the self-bias voltage decreased, the ITO etch rate increased. This suggests that under the plasma conditions used, the ion sputtering effect is not as effective as chemical effects. The increased etch rate is largely due to an increase in the density of the etching species with pressure. As mentioned above, the oxygen in ITO minimizes the etch blocking action of polymer deposition. This is not the case for GaAs. However, this combination of events promotes high selectivity etching of ITO on GaAs above a pressure of 50 mTorr. Figure 3 shows the dependence of ITO and GaAs etch rates on power at 30 mTorr. From Fig. 1, there is no polymer deposition under these conditions. The self-bias voltage varied from 160 V at 10 W to 480 V at 130 W. Etch rates increased for both ITO and GaAs with increasing power. Polymer deposition is inhibited at high power due to ion sputtering.

The etching mechanisms for GaAs and InP in methane plasmas have been explained by the formation of volatile organometallic complexes of Ga or In with the methyl (CH_3) radicals. The removal of As and P is by the formation of arsine and phosphine, respectively.[6-9] Kline *et al.*[10] have demonstrated that CH_3 is also responsible for polymer formation. Therefore in CH_4 plasmas, there is a competition between polymer formation and etching. On inert surfaces such as a SiO_2 mask, polymer deposition rates can be very high. However on active surfaces such as on InP, a combination of chemical reactions and ion-induced effects prevents excessive polymer deposition, even under conditions which favor deposition.[11] In the current work, it is believed that In and Sn are removed as organometallic compounds. The oxygen reacts with adsorbed CH_3 or other such radicals to form CO_x and H_2. Toyoda *et al.*[12] have shown that the density of methyl (CH_3) radicals in CH_4 plasma increases linearly at low pressures, and also linearly with power. It is expected that CH_3 density increases with the concentration of CH_4. Some of these trends are reflected in the ITO etch rates presented above. Departure from these trends for ITO and GaAs can be attributed to the etch blocking action of the deposited thin polymer films.

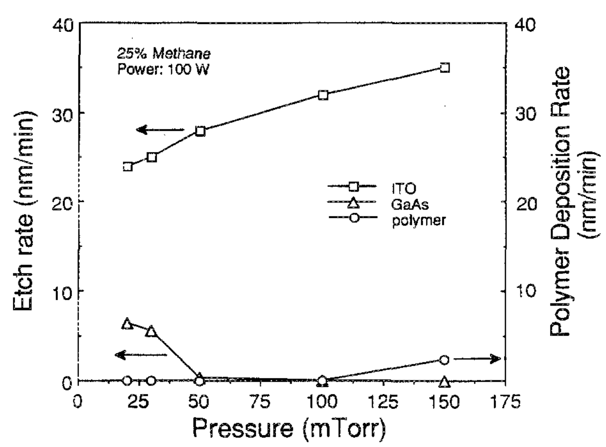


FIG. 2. Etch rates of ITO and GaAs and polymer deposition rate versus pressure.

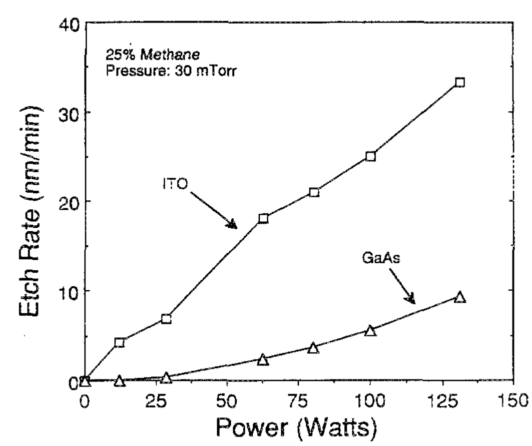


FIG. 3. Etch rates of ITO and GaAs versus power.

B. Etch profiles

Etch profiles of ITO have been studied. Typical etching conditions were gas composition of 25% CH_4, rf power of 100 W, and a pressure between 10 and 80 mTorr. Figure 4(a) shows the etch profile of an 800 nm line etched into ITO for 14 min at 10 mTorr. The Al mask used is evident in the micrograph. The line has been etched 340 nm deep into the 500 nm-thick ITO on GaAs. This gives an etch rate of 24 nm/min, which compares with that in Fig. 2. The self-bias voltage was 450 V. The high energy ion activity is manifested in the trenching observed at the base of the profile. Similar geometry etched at 80 mTorr and 380 V for 14 min is shown in Fig. 4(b). The line has been etched 430 nm deep, which translates to an etch rate of 30 nm/min. The profiles in both figures are essentially anisotropic and are typical of the profiles obtained between the two pressures. Anisotropy in CH_4 plasmas is imparted by ion bombardment rather than sidewall passivation by polymer.[8,13]

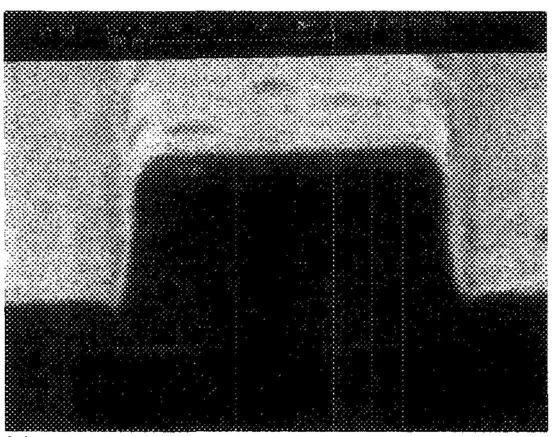
For submicrometer period gratings, electron beam lithography with PMMA resist was used for pattern definition. Here 40 nm-thick Al was lifted off and used as a mask. The 2 μm-period gratings were etched into 250 nm-thick ITO on GaAs at 70 mTorr using the gas composition and power given above. The pressure was chosen to demonstrate the selectivity of the etch process. After etching, the Al mask was removed with a KOH solution. Figure 5 shows the anisotropic etch profile obtained. The selective nature of the etch is illustrated by the smoothness and flatness of the spaces between the ITO lines. This is the surface of the GaAs substrate.

C. MSM Photodetectors

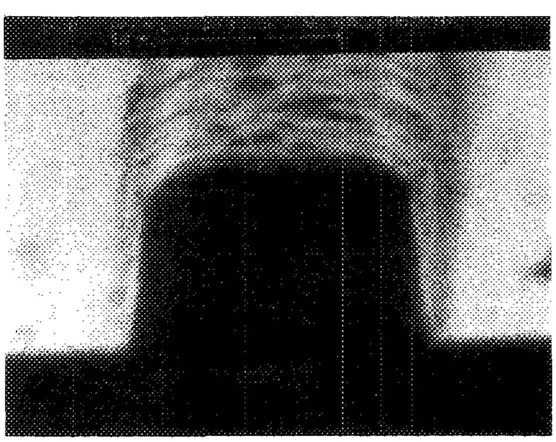
The selective etching process described above has been applied to the fabrication of MSM photodetectors with interdigitated ITO fingers. The detectors were fabricated on a molecular beam epitaxy (MBE) layer grown on semi-insulating GaAs. The layer consisted of 1 μm GaAs buffer, 50 nm graded layer (GaAs to $Al_{0.3}Ga_{0.7}As$), followed by 20 nm $Al_{0.3}Ga_{0.7}As$. 220 nm-thick ITO was deposited on the layer and patterned into MSM devices using photolithography. The photoresist was used as a mask to transfer the MSM pattern into ITO using the selective reactive ion etching conditions delineated for obtaining the anisotropic profile in Fig. 5. Oxygen plasma followed by a rinse in acetone were used to remove the resist mask after etching. Figure 6 is a scanning electron micrograph of a photodetector with 4 μm-period interdigitated ITO fingers. The Al contact pads were fabricated using photolithography and liftoff. An identical device was fabricated using interdigitated Ti/Au (46 nm/200 nm) fingers for comparison. Figure 7 shows the responsivity to 856 nm-wavelength, 50 nW optical radiation as a function of applied voltage for the two types of devices. It is seen that the ITO device is more sensitive than the Ti/Au device due to the higher transmission of optical radiation into the semiconductor. More details on the characteristics of these devices will be published elsewhere.

IV. SUMMARY

The etching characteristics of indium tin oxide (ITO) in methane/hydrogen have been evaluated. An etch rate as high as 30 nm/min and very smooth etched surfaces have been demonstrated. Selective reactive ion etching of ITO on GaAs has been established. The selective etching derives from the polymer deposited on GaAs, which reduces the



(a)



(b)

FIG. 4. SEM micrographs of ITO structures etched in 25%:75%/CH_4:H_2 at 100 W and at (a) 10 mTorr and (b) 80 mTorr. Al mask is seen on top.

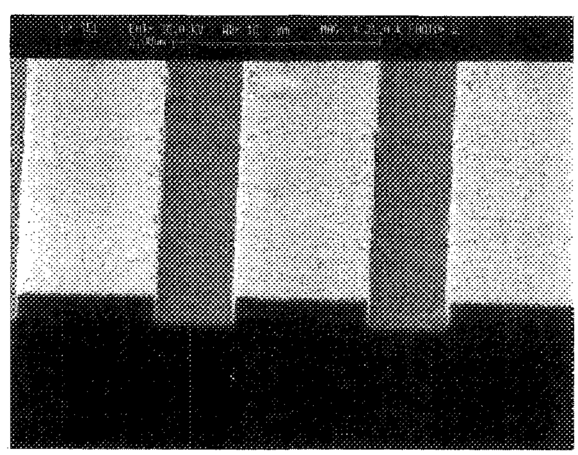


FIG. 5. SEM micrograph of 2 μm-period gratings in ITO selectively etched on GaAs at 70 mTorr.

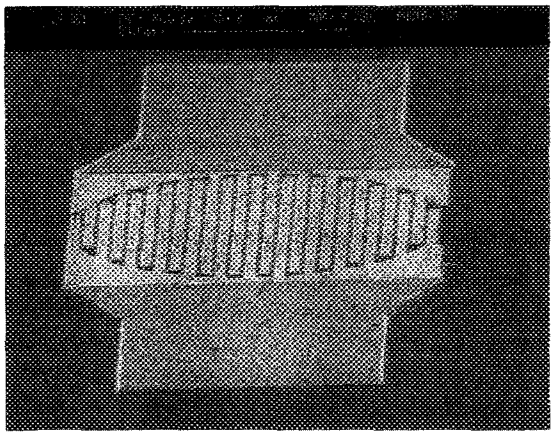


FIG. 6. SEM micrograph of a MSM photodetector with 4 μm-period ITO interdigitated fingers and Al contact pads.

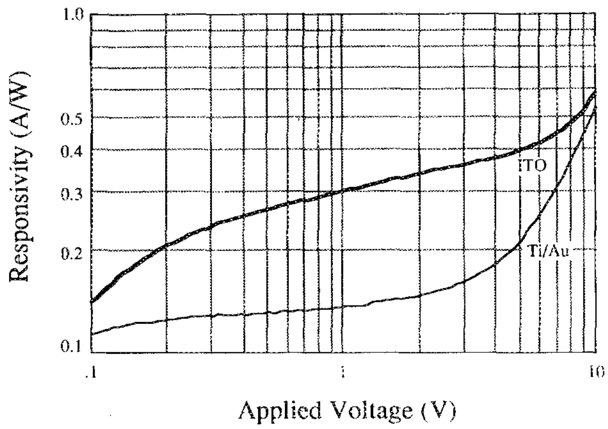


FIG. 7. Responsivities of MSM photodetectors with ITO and Ti/Au fingers.

etch rate of GaAs to zero at high methane concentrations and high pressures. For these conditions very high selectivity ranging from 300 to infinity was achieved. It was shown that submicrometer features with anisotropic etch profiles can be selectively etched in ITO deposited on GaAs. Finally, the etching procedure developed here has been applied to the fabrication of MSM photodetectors. MSM's with patterned ITO fingers demonstrated higher sensitivity than MSM's with Ti/Au fingers.

ACKNOWLEDGMENTS

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